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The impact of optimised coagulation on membrane fouling for coagulation/ultrafiltration process

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ABSTRACT

This work aimed to demonstrate the effect of optimised coagulation on minimise fouling for coagulation–ultrafiltration process. Coagulation as pretreatment has the potential to mitigate fouling and enhance flux. Operating parameters were tested by a matrix of experiments for various mixing conditions and coagulant doses. In coagulation experiments, varied shear forces were applied to generate different floc characteristics in order to assess the effect on membrane fouling. Floc properties were investigated with an optical monitoring technique to identify structure, size and growth of flocs. It was shown that stronger flocs are of advantage for fouling mitigation and that the coagulant dosage is crucial for the performance of filtration. The impact of water quality was assessed using general water quality parameters and organic characterisation techniques to investigate the performance of each treatment step. The treatment efficiency was further assessed based on comparing the molecular size fractions of the organic matter before and after coagulation using a size exclusion chromatography technique. The result confirmed the significance of organic character on treatment performance.

Keywords: Coagulation; Flocculation; Natural organic matter; Photometric dispersion analyser; Ultrafiltration

1. Introduction

Improvement of existing and developing new treatment technologies for supply of high-quality and safe drinking water is a key aim of the water industry. Treatment by coagulation/flocculation–sedimentation–filtration is the most widely applied treatment process, though alternative technologies such as ultrafiltration (UF) in combination with coagulation are becoming more prevalent. Synergistic effects may be expected from each of the treatment process steps. Both processes (coagulation and physical filtration) remove substances of different size and character. Natural organic matter (NOM) is removed mainly by coagulation and the generated flocs are removed by UF. One drawback of the coagulation/UF process is membrane fouling. Further investigation of a range of operational conditions is warranted to enhance coagulation/UF efficiency, incorporating a comprehensive analysis of chemical and physical water quality parameters before

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and after each treatment step, including application of NOM characterisation techniques.

Floc formation during coagulation has a major impact on the fouling behaviour of membranes [1]. When used in pretreatment, coagulation facilitates increased NOM removal and membrane permeability, thereby reducing membrane fouling [2,3]. Consequently, UF treatment operating costs are significantly reduced [4].

Determination of the optimum type and dosage of coagulant is important when establishing an efficient pretreatment regime. Kabsch-Korbutowicz et al. [3] showed that polyaluminium chloride (PACl) is an excellent coagulant in terms of residual aluminium and reduction of NOM, colour and UV absorbance; however, at high doses, a sticky gel-like layer of metal hydroxides forms on the membrane surface, which is resistant to removal [5].

Coagulant dosage should be optimised to ensure the formation of strong flocs, as these are less likely to foul membrane pores through the formation of less dense and more permeable cake layers [6]. In addition, weakly bound floc may fragment due to shear stresses imposed by filtration, and consequently foul membrane pores [7]. Mixing speed also directly influences the maximum size and density of flocs. Numerous other operational parameters can affect floc formation and coagulation including initial coagulant dose, applied shear stresses by agitation, and hydraulic retention time for coagulation and floc formation.

This study aimed to evaluate a coagulation/UF process to understand the impact of different coagulation conditions on UF performance and fouling by assessing optimum floc based on its structure and strength. Coagulant, polyaluminium chloride (PACl) dose and the effect of shear stress by agitation were assessed using flocculation index (FI), which was measured using a photometric dispersion analyser (PDA) [8]. The FI measurement gave rise to two parameters, maximum floc growth rate and variance to facilitate the assessment. This work may aid in establishing a link between floc character and fouling to optimise pretreatment coagulation.

2. Materials and methods

2.1. Materials

2.1.1. Raw water

Raw water was collected from the Murray River at the inlet of the Palmer Water Treatment Plant (WTP), located approximately 70 km east of Adelaide in South Australia. At the time of the investigation, Murray River water at Palmer was considered of high turbidity and had moderate dissolved organic carbon (DOC) (38 NTU and 4.5 mg/L, respectively). The same batch of water was used throughout the study to maintain consistent raw water quality with water quality analyses prior to the experimental runs.

2.1.2. Coagulants

An inorganic pre-polymerised coagulant, PACl, was used in this study. A working solution of PACl (14.38 g/L aluminium, Megapac 10, Omega Chemicals, Australia) in 500 mL ultrapure water (Milli-Q) was prepared for all experiments. The aluminium concentration of the PACl working solution was 0.38 g/L.

2.1.3. Membrane and membrane module

The UF membrane module was previously described [9] and was a custom potted hollow fibre membrane that operated in outside-to-inside configuration. The UF membrane had a nominal pore size of 0.02 μm and was made from hydrophobic polyvenylidene fluoride (PVDF). The test rig utilised a bundle of ten 10 cm fibres, each fibre having an outer diameter of 1 mm (filtration area 31.4 cm^2). For all experiments, the same set of membranes was used. Membranes were thoroughly backwashed with air and ultrapure water, and cleaned using citric/sulphuric acid at pH 2 followed by sodium hydroxide at pH 10 and finally rinsed with ultrapure water between experiments to a consistent starting flux.

2.1.4. Test rig setup

A schematic diagram of the coagulation/UF test rig is shown in Fig. 1. Raw water was pumped into a mixing container at 90.4 mL/min and bypass recirculated water was pumped back to a raw water tank. The flow into the mixing container was then regulated with two upstream valves. In the mixing container (approximately 900 mL), a peristaltic pump delivered coagulant at a constant flow of 8.0 mL/min and mixing was driven by a flat paddle agitator. From the mixing container, the water flow was driven by gravity into the settling container. The settling container volume was 1 L (hold 1 L of treated water), this volume was chosen to mimic the holding tank of the submergible membrane system at the Palmer WTP with the scaled down flow rate. The water was pumped with a peristaltic pump into the membrane pressure cell, which had a volume of 841 mL. Before

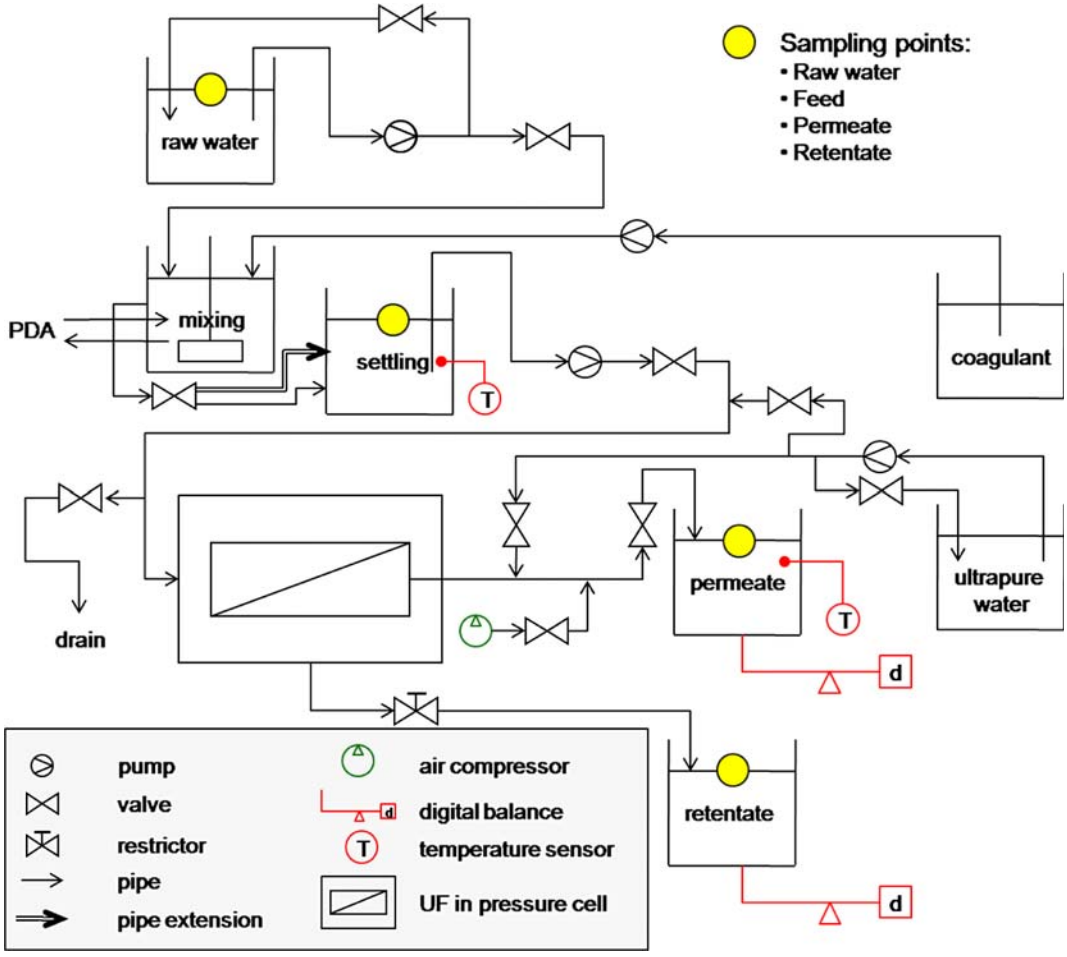

Fig. 1. Setup schematic. The ○ spheres indicate the sampling points for raw water, feed, permeate and retentate.

the water was collected in a retentate container, a restrictor produced feed pressure on the membrane to a constant 1.6 bar. The weight of the collected retentate and permeate was measured with a top pan balance (UW6200H, Shimadzu, Japan). Flocculation time was 9 min, whilst settling time was 11 min. The flux decline could be estimated from a decreasing accumulation of permeate, which was continuously recorded.

2.2. Experimental procedure

2.2.1. Optimisation of the coagulation pre-treatment process

The PACl dose range was determined initially by jar testing. A variable speed six paddle gang stirrer with 7.5 cm diameter flat paddle impellers and square jars (B-Ker^2, Phipps & Birds, USA) were used. A commonly used condition of 1 min of flash mixing at 200 rpm was reduced to 20 rpm for 14 min which was selected. The samples were then allowed to settle for 15 min. The settled water was filtered through an 11 μm pore size paper filter (Whatman No.1, Whatman International, UK) to simulate the effects of rapid media filtration [10]. The use of paper filter would not produce the same result as the rapid sand filter but this procedure can provide consistent result for the laboratory test. The optimum coagulant dose (14 mg/L PACl) of the raw water was determined based on ultraviolet absorption at 254 nm (UV_{254}) reduction by a set of six jar tests with a range of coagulant dosages. The full procedure is described in Staaks et al. [10]. The enhanced dose was selected to be doubled (28 mg/L PACl) to represent a better treatment condition with better treated water quality to compare with the conventional dose.

Using the coagulation/UF test rig, two operational parameters, PACl dose and mixing speed were studied. The optimum and enhanced dose were investigated and flocculation index (FI) monitored. Two

mixing speeds were employed during coagulation, 50 and 150 rpm.

2.2.2. Flocculation index measurement

FI was monitored by PDA. The PDA (PDA 2000, Rank Bros Ltd., UK), is a monitoring instrument for analysis of flowing suspensions [8]. The PDA was connected via flexible tubing to the mixing chamber during testing (Fig. 1). A peristaltic pump circulated the sample water at 21.6 mL/min. The pump was located after the PDA to minimise deterioration of the floc. The intensity of transmitted light (sourced from a light emitting diode at 850 nm wavelength) fluctuates concurrently with the number of particles. Two parameters, maximum growth rate (described as the coordinates of the point with maximum floc growth) and variance, derived from the FI curve were used to assess the coagulation performance.

The first parameter, maximum growth rate, was determined using several computational steps to derive the actual growth rate. The output data of the PDA creates the FI values with the appropriate time in seconds. A sigmoid function is generated with a curve fitting tool.

$$f(x) = a + \frac{b}{e^{\frac{-(x-c)}{d}}} \quad (1)$$

where a, b, c, d = computed variables by curve fitting tool.

The resulting function was derived using WolframAlpha™ software (Wolfram Research, Inc., USA). The first derivation was in turn used as input data into the software. The maximum value of the first derivation is the point with maximum growth rate of the anti-derivative i.e. maximum growth occurs at the point of inflexion of the sigmoid function.

The second parameter, variance, was introduced by Hopkins and Ducosto [11] and can be used to assess floc structure differences. This parameter is based on the fluctuations of the FI data after the growth of floc has reached a plateau, and is calculated based on the following equation [11]:

$$\text{Variance} = \frac{\sum_{i=1}^{n}[(\text{FI} - \text{average FI})_i^2 \cdot \text{time}_i]}{\sum_{i=1}^{n}\text{time}_i} \quad (2)$$

2.3. Analytical methods

2.3.1. General water quality analysis

UV_{254} and true colour (456 nm) were determined using a UV/Vis spectrophotometer (Evolution 30, Thermo Scientific, USA) with a 1 cm and a 5 cm quartz cell, respectively. True colour measurement is expressed in Hazen Unit (HU) by using platinum/cobalt standard at 50 HU for calibration and applying the reported method [12]. DOC concentrations were measured using a total organic carbon analyser (Sievers 900, GE Analytical Instruments, USA). Samples, excluding those intended for turbidity measurement, were filtered through a pre-rinsed 0.45 μm syringe filter. Turbidity was measured using a Hach 2100AN turbidimeter (Hach, USA) and is expressed in nephelometric turbidity units (NTU).

2.3.2. Liquid Chromatography–Organic Carbon Detection

A Liquid Chromatography–Organic Carbon Detection (LC–OCD) system was used (Model 8, Huber, Germany). Samples were filtered through a 0.45 μm filter. Further details of the analytical procedure and conditions are described in Liu et al. [13]. The results were presented as μg/L of carbon of the five fractions: biopolymers (>20,000 Da), humic substances (1000 Da), building blocks (300–500 Da), low-molecular weight neutrals (<350 Da) and low-molecular weight acids (<350 Da).

3. Results and discussion

3.1. Impact of coagulation conditions on flocculation behaviour

The PDA data showed the aggregation and disaggregation of flocs. As the FI represents a relative value (ratio), a variance comparison can be derived from the PDA data. Ching et al. [14] and Hopkins and Ducosto [11] have applied variance calculations; however attained PDA parameters depend on the location of coagulation and the type of coagulation (i.e. with or without settling). In our study, two parameters were established depending on the sampling location where flocculation was measured in the mixing container. Each parameter depended on the type of coagulation as well as initial mixing followed by constant mixing. The first parameter concerns the growth rate of floc during initial mixing. The second parameter concerns the type of floc. The results for maximum growth rate for coagulation and variances are presented in Fig. 2 for both the optimum and enhanced doses at two mixing speeds.

Differences between optimum and enhanced dosage were observed (Fig. 2). Maximum growth rate was higher with enhanced dosage, and increased substantially with 150 rpm agitation. Higher agitation in

combination with enhanced dosage caused the fastest maximum growth rate. This may be attributed to higher availability of PACl due to enhanced dosage and higher speed agitation facilitating greater particle collision frequency, thus reducing reaction time [11].

Variance results were divided by agitation speed as presented in Fig. 2(b). Two major findings were apparent: (1) variance was higher at low agitation speed (50 rpm). (2) Variance from the enhanced dose was higher than from optimum dose. In mathematical terms, the variance (Eq. (2)) gives a derivation of the FI value. It can be concluded that a large variance indicates overall larger size and wider size range of flocs [11]. At increased agitation speed, variance was smaller indicating a more homogeneous floc suspension. The smaller variance for high agitation speed shown in the results allows the strength of the floc to be clearly brought into context breaking the floc using stronger physical forces that cause surface erosion and large-scale fragmentation of floc [7]. Large variance also indicates larger, weaker flocs. The higher variance observed with enhanced coagulant dose may be caused by the formation of larger flocs that are more susceptible to breakage at higher agitation speeds. Flocs formed under high coagulant dosage tend to have open floc structures that are weaker, easily fractured and may generate a wider distribution of floc sizes [11]. As a result, a greater variance does not necessarily mean a weaker floc when comparing different coagulant doses. Floc formed at high agitation speed and high coagulant dosage needs to withstand stronger physical force than smaller flocs formed by lower coagulant dose. This suggests that larger and stronger floc was initially formed at high agitation for the enhanced coagulant dosage.

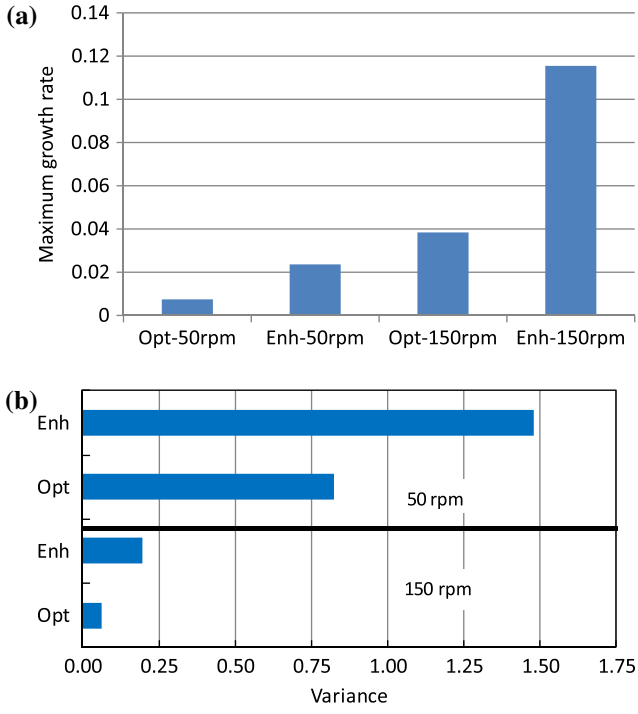

Fig. 2. (a) Maximum growth rate at different testing conditions; Opt. = optimum dose (14 mg/L PACl), Enh = enhanced dose (28 mg/L PACl) and (b) variance at different testing conditions.

Variance was found to be a parameter that might give crucial size and strength information about floc structure. The promising nature of this parameter is the ease with which it can be calculated and the implication for the parameter to be used in online monitoring of coagulation processes. These conclusions, however, are based on a single water source. Variance may be specific to each water source implying that to employ online monitoring, site specific calibration may need to be performed.

3.2. Turbidity, colour, UV_{254} and DOC removal

In the coagulation/UF process, the largest proportion of colour was reduced by coagulation. In total, approximately 80% of chromophores can be removed by the coagulation/UF process (calculated based on Table 1). It is evident that the membrane removes nearly all turbidity, with a residual of only 0.14 NTU. These are crucial values that guarantee the integrity of the membrane. From Table 1, it may be observed that the relative reduction of colour by coagulation is higher than relative reduction of turbidity; the opposite if observed for UF.

The organic carbon concentrations for the test conditions with optimum coagulant dose are presented in Table 1. As expected the removal of DOC was greater using coagulation (38%) than when using UF without coagulation.

3.3. Biopolymer fouling

As DOC was poorly removed by UF in this investigation, LC–OCD analysis was used to assess removal of biopolymers, as this type of organics have been shown to foul UF membranes [2]. Biopolymers were removed very well by coagulation as indicated by the difference in organic carbon concentration of raw water and feed (Tables 1 and 2). Both testing conditions showed more than half of the biopolymers were removed (Table 2). The least biopolymer removal was observed at optimum coagulant dose. The UF rejected a further 44% of the biopolymers with coagulant optimum dose and 45% of biopolymers with enhanced

Table 1
The removal of turbidity, colour, UV_{254} and DOC for the coagulation/UF process. Two coagulant doses, optimum and enhanced, were used with 50 rpm mixing

		Turbidity (NTU)	Colour (HU)	UV_{254} (cm^{-1})	DOC (mg/L)
	Raw	61.7	18	0.140	4.5
Optimum dose	Feed	36.6	6	0.044	2.8
	Permeate	0.14	4	0.040	3.4[a]
	Retentate	30.6	8	0.042	3.0
Enhanced dose	Feed	34.7	3	0.032	2.2
	Permeate	0.14	3	0.034	2.2
	Retentate	29.9	3	0.032	2.2

Measurement standard deviation: turbidity (±6%), colour (±4%), UV_{254} (±4%), DOC (±3%).
[a]This DOC concentration is believed to be inaccurate (higher than the feed). This could be due to measurement issue. This unusual data point would not affect the overall interpretation.

Table 2
LC–OCD analysis of coagulated waters using optimum and enhanced doses

Approximate MW (g/mol)	≫20,000	1000		300–500	<350	<350
Fraction	Biopolymers	Humic substances		Building blocks	LMW neutrals	LMW acids
Unit	ppb-C	ppb-C	g/mol (M_n)	ppb-C	ppb-C	ppb-C
Raw water	198	1,099	545	694	2,185	385
Opt dose—Feed	93	831	498	487	1,409	145
Opt dose—Permeate	52	834	461	418	744	19
Enh dose—Feed	77	672	519	873	1,809	1,727
Enh dose—Permeate	42	832	412	553	2,467	715

Notes: MW = molecular weight; LMW = lower MW; ppb-C = parts per billion carbon; M_n = average MW; Opt dose = optimum dose; Enh dose = enhanced dose. When comparing the feed with permeate data pairs, apparently some values are higher in the permeate than in the feed, e.g. LMW neutrals in the Enh set, this could be due to minor contamination during the experiment or analysis. However, this discrepancy did not affect result interpretation as the purpose of this test was investigating membrane fouling from biopolymers.

coagulant dose. Higher molecular weight biopolymers were most likely physically removed by the membrane or entrained in the cake layer [15]. Humic substances, however, are of lower molecular weight [13] and at 1000 Da and less, minimal physical removal effect occurred following UF. Liu et al. [6] found that in water with a high humic concentration, flocs with higher fractal dimension and lower effective density caused higher porosity of cake layer and thus higher UF flux. The average molecular weight for the analysed molecules was around 500 Da. No great variation was observed between carbon concentration of feed and permeate suggesting removal from raw water was by coagulation with an average efficiency of 34%. The building blocks were neither removed by coagulation nor by UF. Removal of the low-molecular weight (LMW) neutral fraction was not observed for the enhanced dose conditions in contrast to the optimum dose which removed nearly 50% of the LMW neutral fraction. The LMW acids showed divergent results, which cannot be explained by the treatment processes. Both maximum growth rate and variance showed greatest values when biopolymer concentration was minimised by the enhanced dose.

3.4. Flux decline

The results for specific flux normalised for temperature variation, J_v/J_0, are summarised in Fig. 3. J_0 was defined as the initial instantaneous flux of the raw water while J_v was defined as the flux of the coagulated water. Fig. 3(a) and (b) shows the normalised flux for optimum and enhanced coagulant doses over a 120 min period.

The flux decline reveals the fouling behaviour of the membrane. At 150 rpm, the specific flux values were most favourable for both the optimum dose and the enhanced dose, and flux decline was less rapid.

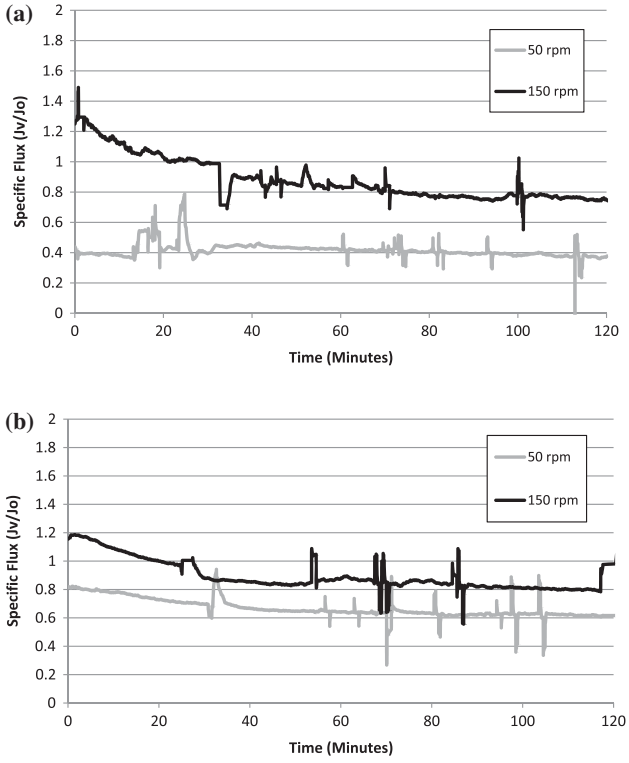

Fig. 3. (a) Normalised specific flux for optimum dose and (b) normalised specific flux for enhanced dose.

Considering that the flux was less declined at 150 rpm as compared with the 50 rpm, the membrane was fouling less severely. Permeability at 150 rpm decreased substantially within the first 30 min, while fouling behaviour at 50 rpm only decreased slightly over the whole experiment.

Best results for minimisation of flux decline were achieved at high agitation (150 rpm) at either optimum or enhanced doses. PDA measurements indicated greater maximum growth rate and lower variance at this time. As a result of the coagulation of biopolymers discussed above, specific flux decline was minimised when biopolymer concentration was also minimised.

4. Conclusions

This work revealed various benefits and challenges of treating South Australian river water using the coagulation/UF process. The study demonstrated that the PDA parameters of maximum growth rate and variance allow investigation of floc growth and floc structure. Determining 'maximum growth rate' is useful in terms of optimising the coagulation process parameters, particularly initial mixing times. Variance is of special interest, since relative strength as well as size of floc can be estimated on a continuous basis. As a result, variance may be employed for online monitoring of flocs, determining coagulant dose and applied agitation speed. Stronger flocs are proposed to be advantageous for membrane filtration as these bind more particulates in the water and are less likely to form a metal hydroxide gel layer on the membrane. Determining the strength of the floc may be used to assess the right conditions for coagulation as pre-treatment prior to UF.

LC–OCD gave precise information about the removal of biopolymers and humic substances. Biopolymers were removed by coagulation at a maximum of 64% and UF removed a further 44–45%. Humic substances were removed by coagulation at an average of 34%.

Beneficial operating parameters were identified under different test conditions. Best results for minimisation of flux decline were achieved at medium agitation (150 rpm) at either optimum or enhanced doses. PDA measurements indicated greater maximum growth rate and lower variance at this time.

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